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(71) **BASF AKTIENGESELLSCHAFT,
D-67056, LUDWIGSHAFEN, XX (DE).**

(72) **KELLER, PETER (DE).
BINDER, HORST (DE).
BLUM, RAINER (DE).**

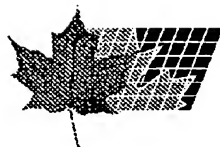
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(54) **MATERIAUX ET PREPARATIONS DURCISSEES PAR UN RAYONNEMENT HAUTE ENERGIE ET/OU PAR LA CHALEUR**

(54) **RADIATION-HARDENING AND/OR HEAT-HARDENING SUBSTANCES AND PREPARATIONS**

(57)

The invention relates to radiation-hardening and/or heat-hardening substances and preparations with an oligomer or polymer basic structure, comprising at least one terminal or lateral vinyl ether group (a) and at least one group (b) that is different from said vinyl ether groups (a) and co-reacts with said groups (a), whereby, on average, at least one vinyl ether group (a) and one co-reactive group (b) are present for each oligomer or polymer molecule. The invention also relates to preparations containing the inventive material and to the uses of said preparation in or as a binder for liquid enamelling systems, coating powders, or as or in adhesives, casting agents and impregnating agents for electronics or electro-technics and for the production of shaped bodies.



- (72) BLUM, RAINER, DE
(72) KELLER, PETER, DE
(72) BINDER, HORST, DE
(71) BASF AKTIENGESELLSCHAFT, DE
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PCT
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**INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)**

<p>(51) Internationale Patentklassifikation ⁷ : C08F 299/02, C08G 18/67</p>	<p>A1</p>	<p>(11) Internationale Veröffentlichungsnummer: WO 00/08081</p> <p>(43) Internationales Veröffentlichungsdatum: 17. Februar 2000 (17.02.00)</p>
<p>(21) Internationales Aktenzeichen: PCT/EP99/05646</p> <p>(22) Internationales Anmeldedatum: 4. August 1999 (04.08.99)</p> <p>(30) Prioritätsdaten: 198 35 913.6 7. August 1998 (07.08.98) DE</p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF AK- TIENGESellschaft [DE/DE]; D-67056 Ludwigshafen (DE).</p> <p>(72) Erfinder; und (75) Erfinder/Anmelder (nur für US): BLUM, Rainer [DE/DE]; Rüdigerstrasse 64, D-67069 Ludwigshafen (DE). KELLER, Peter [DE/DE]; Mozartstrasse 9, D-66583 Spiesen-Elversberg (DE). BINDER, Horst [DE/DE]; Schwimmbadstrasse 24, D-68623 Lampertheim (DE).</p> <p>(74) Anwalt: ISENBRUCK, Günter, Bardehle, Pagenberg, Dost, Altzburg, Geissler, Isenbruck, Theodor-Heuss-Anlage 12, D-68165 Mannheim (DE).</p>	<p>(81) Bestimmungsstaaten: CA, CN, JP, KR, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i></p>	
<p>(54) Title: RADIATION-HARDENING AND/OR HEAT-HARDENING SUBSTANCES AND PREPARATIONS</p> <p>(54) Bezeichnung: DURCH ENERGIEREICHE STRAHLUNG UND/ODER THERMISCH HÄRTBARE STOFFE UND ZUBEREITUN- GEN</p> <p>(57) Abstract</p> <p>The invention relates to radiation-hardening and/or heat-hardening substances and preparations with an oligomer or polymer basic structure, comprising at least one terminal or lateral vinyl ether group (a) and at least one group (b) that is different from said vinyl ether groups (a) and co-reacts with said groups (a), whereby, on average, at least one vinyl ether group (a) and one co-reactive group (b) are present for each oligomer or polymer molecule. The invention also relates to preparations containing the inventive material and to the uses of said preparation in or as a binder for liquid enamelling systems, coating powders, or as or in adhesives, casting agents and impregnating agents for electronics or electro-technics and for the production of shaped bodies.</p> <p>(57) Zusammenfassung</p> <p>Die Erfindung betrifft durch energiereiche Strahlung und/oder thermisch härtbare Stoffe mit einer oligomeren oder polymeren Grundstruktur, die jeweils end- und/oder seitenständig mindestens eine Vinylethergruppe a) und mindestens eine von den Vinylethergruppen a) verschiedene, mit den Gruppen a) coreaktive Gruppe b) aufweisen, wobei im Durchschnitt mindestens eine Vinylethergruppe a) und eine coreaktive Gruppe b) pro Oligomer- oder Polymermolekül vorhanden sind. Die Erfindung betrifft auch Zubereitungen, die den erfindungsgemäßen Stoff enthalten und Verwendungen der Zubereitung als oder in einem Bindemittel für flüssige Lacksysteme, für Pulverlacke, als oder in Klebstoffen, Gieß- und Tränkmitteln für die Elektronik und/oder Elektrotechnik und für die Herstellung von Formkörpern.</p>		

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RADIATION-HARDENING AND/OR HEAT-HARDENING
SUBSTANCES AND PREPARATIONS

The invention relates to substances and formulations curable thermally and/or by high-energy radiation and to their uses in accordance with the invention.

10 The starting point for the present invention were considerations in the field of UV-curable coating materials for use in liquid form, and powder coating materials. Such coating systems are continually acquiring more fields of use on the grounds of reduced solvent consumption. A major problem with known UV coating materials, however, is the inhibiting effect of atmospheric oxygen on curing at the film surface. To overcome this inhibition requires lamps with very high energy density, and accelerated curing by means of amine coinitiators. These amines are frequently the cause of odor nuisance.

20 In the case of UV powder coating materials, in addition, further problems arise from the contradictory requirements for good blocking resistance of the powders on storage and good leveling of the melted coating film. For good blocking resistance, the glass transition temperature and melting point should be as high as possible, whereas for good leveling, and to permit use on heat-sensitive substrates, they should be as low as possible, in order to prevent a curing reaction before optimum surface smoothness has developed and in order to prevent substrate damage. Likewise for the purpose of improving the surface smoothness, the melt should have a low viscosity and the reaction should set in only after a delay period. These concepts are difficult to realize with powder coating materials whose curing is based on one of the known, thermally activated reactions between resin and hardener, e.g., polyepoxy resin and dicarboxylic acid hardener, since a viscosity-increasing reaction sets in simultaneously with the melting process. In the case of radiation-curable powder coating materials, on the other hand, it should be possible
30 to separate the melting process from crosslinking. In order to meet this requirement, various attempts have been disclosed in the prior art.

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US-A-4,129,488 and US-A-4,163,810 disclose UV-curable powder coating materials having specific spatial arrangements of ethylenically unsaturated polymers. Here, the binder consists of an epoxy-polyester polymer in which the epoxy adduct is arranged spatially such that by means of a linear polymer chain it is at a distance from the polyester adduct. In addition, the polymer comprises a chemically bonded photoinitiator.

EP-A 0 650 978, EP-A 0 650 979 and EP-A 0 650 985 disclose copolymers whose essential constituent is a relatively high fraction of monomers having the structural unit of methacrylic acid. These monomers can be used as binders for UV-curable powder coating materials, and feature a relatively narrow molecular weight distribution.

EP-A 0 410 242 discloses binders for UV-curable powder coating materials, consisting of polyurethanes which have specific (meth)acryloyl groups, can be crosslinked without crosslinker components or peroxides, and are therefore stable on storage. Crosslinking by UV irradiation requires the addition of photoinitiators.

EP-A 0 636 669, furthermore, discloses a UV-curable binder for powder coating materials which consists of unsaturated polymers, which can include cyclopentadiene, and a crosslinking agent which has vinyl ether groups, vinyl ester groups or (meth)acrylic groups.

WO-A-93/25596 discloses polyacrylates, for use as automotive topcoats, which are functionalized with double bonds in a wide variety of ways.

DE-A 42 26 520 discloses liquid compositions comprising unsaturated polymer, in the form of unsaturated polyesters, and compounds containing (meth)acryloyl groups and/or vinyl ether groups. These compositions can be crosslinked both by means of free-radical initiators and by means of radiation curing, and are used as binders for coating materials. In the case of crosslinking by UV radiation it is necessary to add photoinitiators.

With the UV coating materials of the cited prior art, problems arise as a result of the need to employ coinitiators, generally amines, in order to provide high photosensitivity and to overcome the known oxygen inhibition of the surface. The

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elimination products of these photoinitiators remain in the cured coatings and are the cause of odor nuisance.

5 In addition, EP-A-0 322 808 has disclosed a prior art which reveals a liquid binder, curable by means of high-energy radiation, which consists of a mixture of an ethylenically unsaturated polyester component, which may also include an ethylenically unsaturated polyester oligomer, and a nonpolymerized vinyl ether component. In this case, the vinyl ether component is selected such that per molecule of the vinyl ether component it contains on average at least two vinyl
10 ether groups which are able to react with the ethylenic double bonds of the polyester component.

Against the background of this prior art, it is an object of the present invention to provide substances and formulations whose use in coating systems which are
15 curable thermally and/or by means of high-energy radiation is unaccompanied by oxygen inhibition of the film surface, so that it is possible to forego the use of malodorous amines and other coinitiators, and which can also be employed more broadly.

20 We have found that this object is achieved by substances with an oligomeric or polymeric substructure having in each case terminally and/or laterally at least one vinyl ether group a) and at least one, preferably copolymerizable group b) which is different from the vinyl ether groups a) but is coreactive with the groups a), there being on average at least one vinyl ether group a) and one coreactive group b) per
25 oligomer or polymer molecule.

Coating systems which comprise such substances surprisingly show high UV reactivity and no oxygen inhibition of the surface when cured in air. This has the advantage that it is possible to forego the use of amines and other coinitiators.

30 Also possible is curing to a B-stage, i.e., to a partially cured state in which the curing is interrupted and can be started again later.

In connection with the substances of the invention, mention should be made of the
35 problem, known per se to the skilled worker, that in the course of the customary polymer synthesis, which takes place under statistical reaction conditions, and/or in the case of polymer-analogous functionalization, it is also possible for polymer

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molecules to be formed which are functionalized only in one way, e.g., with the vinyl ether groups a), or which are not functionalized at all. Since such polymeric substructures with little functionalization or none whatsoever may adversely effect the properties of the polymers of the invention, it is preferred to direct the preparation process such that minimal fractions of such minimally functionalized or completely unfunctionalized polymeric substructures are formed. Methods suitable for this purpose are known to the person skilled in the art of polymers. They include the use of excesses of substances which if unreacted can be separated off again later, or, if desired, the residence of the excess in the finished coating binder. It has been found that any residual fractions which nevertheless remain have essentially no adverse effect on the success of the invention when using the claimed binders.

The outstandingly high UV reactivity which is observed when the substances of the invention are used in powder coating materials curable thermally and/or by means of high-energy radiation, which is unaccompanied by oxygen inhibition of the surface, is attributed to the fact that functionalization of the polymeric substructure in the substances of the invention permits self-crosslinking to take place, whereas in the prior art the compositions are mixtures of substances which must only be crosslinked with one another.

The schematic structural principle of the substances of the invention can be illustrated as follows:

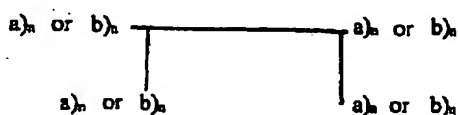


Fig. 1

n = 0 - 6

In accordance with the structural principle depicted, the functional groups a) and b) can be linked to the oligomeric or polymeric substructure at the same point and/or different points, and they may arbitrarily terminate this substructure. The functional groups a) and b) may also be present more than once on the same group. Thus, for example, two glycidyl methacrylates can react at a terminal NH_2 group, or one molecule of ethanolamine divinyl ether at a terminal epoxy group. Furthermore, polymeric substructures having two or more OH groups laterally or terminally at the same site can be vinylated. The value for n here is between 0 and 6, preferably 1 or 2.

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The oligomeric or polymeric substructure can be formed by C-C linkages which have double and/or triple bonds and/or are selected from ester, ether, urethane, amide, imide, imidazole, ketone, sulfide, sulfone, acetal, urea, carbonate and siloxane linkages.

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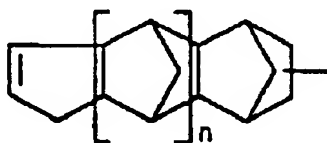
In addition, the oligomeric or polymeric substructure may be linear, branched, annular or dendrimeric.

10

The binders of the invention are obtained preferably by polymer-analogous reaction of functional polymers with compounds having functional groups a) or b) and at least one further group which are able to react with the functional groups of the oligomeric or polymeric substructure.

15

Particularly suitable coreactive, preferably copolymerizable, functional groups b) are maleate, fumarate, itaconate (meth)acrylate, allyl, epoxy, alkenyl, cycloalkenyl, vinylaryl and cinnamate groups and/or preferably structural units of the formula I.



n= 0-10

I

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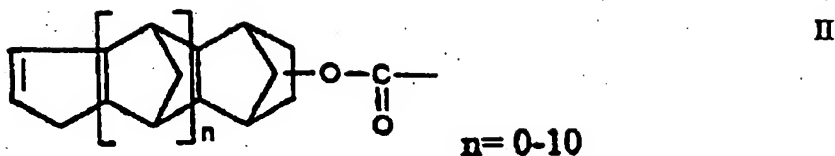
When structural units of the formula I are used as functional group b), the coating systems are notable during preparation for low heat sensitivity and yet good stoving curability under atmospheric oxygen, for short curing times with combined use of heat and UV light, for good blocking resistance of the powders on storage, in the case of powder coating materials, and for very good surface smoothness of the resultant coatings.

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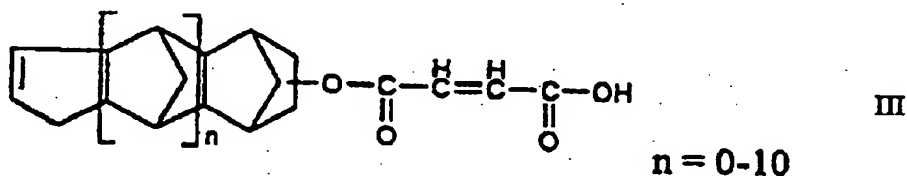
In one preferred embodiment, the structural units of the formula I in the coreactive groups b) can be incorporated in the form of esters of (oligo)dihydrodicyclopentadienol with monofunctional or polyfunctional carboxylic acids of the formula II.

30

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An important polymer class of the invention is that of the **epoxy resins**. Suitable substructures are multiply epoxy-functional polymeric, oligomeric or monomeric compounds of the type, for example, of the bisphenol A epoxy compounds or bisphenol A epoxy resins, by reaction with compounds that are reactive with epoxy groups. The epoxy groups can be functionalized with compounds having vinyl ether groups a) and groups b) coreactive with them and contain at least one further group which is able to react with epoxides. Examples of compounds of this kind according to the invention are the products of partial reactions of conventional commercial epoxy resins with (meth)acrylic acid and/or compounds of the formula III below and an aminovinyl compound, such as aminobutyl vinyl ether or diethanolamine divinyl ether, or the reaction products of polyacrylates with copolymerized glycidyl (meth)acrylate with such compounds, or the reaction products of polyurethane resins obtained with such compounds with the additional use of hydroxy-functional epoxy compounds, an example being glycidol (2,3-epoxy-1-propanol).



Polyurethane resins constitute a further important class of polymer according to the invention, and are obtained by reacting polyfunctional isocyanate compounds with acrylates and vinyl compounds, hydroxyacrylates or aminoacrylates, and hydroxyvinylates or aminovinylates, with or without the additional use of further, isocyanate-reactive compounds, such as hydroxy compounds.

Isocyanate compounds which can be used include commercially customary and conventional compounds, such as tolylene diisocyanate (TDI), 4,4'-methylenedi(phenyl isocyanate) (MDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HMDI), further C₂-C₁₂ alkylene diisocyanates, further

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- C₂-C₁₂ cycloalkylene diisocyanates, naphthalene diisocyanates, further alkaryl diisocyanates, such as phenylene diisocyanates, biphenyl diisocyanates, and the various positional isomers of these compounds. Also suitable are the derivatives of these isocyanates that are of higher isocyanate functionality, the products of biuretization and isocyanuratization, such as the isocyanates oligomerized or trimerized by way of uretdione groups, and the higher isocyanates obtainable from the simple isocyanates mentioned above by dimerization or oligomerization with amines or water.
- 10 Polyisocyanates which contain diisocyanurate groups are of particular importance. Particular mention may be made here of the trimerization products of the above-mentioned diisocyanates.

To prepare the binders of the invention, these isocyanates, or mixtures thereof, are reactive with compounds which are reactive with the isocyanates and which in addition to the isocyanate-reactive groups also contain the groups a) and b). It is also possible to make use in addition of isocyanate-reactive compounds which do not contain the groups a) or b). The compounds to be reacted with the isocyanates can be singly or multiply reactive with isocyanates and can be linear, branched, aromatic, cycloaliphatic, araliphatic or heterocyclic and/or can be substituted in any desired manner. Examples are C₁-C₂₀ hydroxyalkyl vinyl ethers, such as hydroxyethyl monovinyl ether, hydroxybutyl monovinyl ether, cyclohexanedimethanol monovinyl ether, hexanediol monovinyl ether, ethylene glycol monovinyl ether, propylene glycol monovinyl ether and polyalkylene glycol monovinyl ethers, and also diethanolamine divinyl ether, aminopropyl vinyl ether, C₁-C₂₀-hydroxyalkyl (meth)acrylates, such as hydroxyethyl acrylate, hydroxybutyl acrylate and also polyalkylene glycol monoacrylates, allyl alcohol, dihydrodicyclopentadienol, hydroxyl-containing adducts of dicyclopentadienol (DCPD) with glycols, as per formula scheme V below, ethylene glycol, polyethylene glycols, propylene glycol, polypropylene glycols, butanediol isomers, hexanediol, neopentyl glycol, trimethylolpropane, glycerol, pentaerythritol, unsaturated hydroxy compounds, such as allyl alcohol, partially etherified polyfunctional hydroxy compounds, examples being trimethylolethane monoallyl ether, trimethylolethane diallyl ether, trimethylolpropane monoallyl ether, trimethylolpropane diallyl ether, pentaerythritol monoallyl ether, pentaerythritol diallyl ether, alkylenediols, such as 2-butene-1,4-diol, and alkoxylated alkylenediols, preferably ethoxylated and propoxylated 2-butene-1,4-diol having a

degree of alkoxylation of from 1 to 10 alkylene oxide units per mole of 2-butene-1,4-diol.

5 The selection and combination of the particular starting compounds desired depends on the desired properties of the substances to be prepared from them. The required molecular weight and, if desired, the viscosity can be established by additionally using monofunctional compounds. The abovementioned measures, and the selection of a suitable polymerization technique with or without the additional use of solvents, and the control of the polymerization by means of catalysts, are possible for the skilled worker on the basis of his or her expert knowledge.

10 For the purposes of this invention, the term polyurethanes is intended to include not only those compounds whose main chain is linked by way of urethane linkages but also those compounds which have ester or ether chain links, i.e., the polyester urethanes and polyether urethanes.

15 Saturated and unsaturated polyester resins functionalized in accordance with the invention with groups a) and b) constitute a further important polymer class for the binders of the invention. Suitable for synthesizing the polyester resins are the customary and known carboxylic acids having > 2 carboxyl groups and/or their anhydrides and/or their esters, and hydroxy compounds having > 2 OH groups. It is also possible to use monofunctional compounds in addition in order, for example, to regulate the molecular weight of the polycondensates.

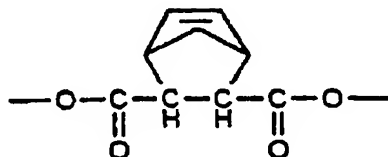
25 Examples of suitable carboxylic acid components are α,β -ethylenically unsaturated carboxylic acids, such as maleic acid, maleic anhydride, fumaric acid, itaconic acid, citraconic acid, saturated aliphatic carboxylic acids and their anhydrides, such as succinic acid, adipic acid, suberic acid, sebacic acid, azelaic acid, naturally occurring fatty acids and polymerized naturally occurring fatty acids, such as linseed oil fatty acid, dimeric linseed oil fatty acid and polymeric linseed oil fatty acid, castor oil, castor oil fatty acid, saturated cycloaliphatic carboxylic acids and their anhydrides, such as tetrahydrophthalic acid, hexahydrophthalic acid, endomethylene-tetrahydrophthalic acid, norbonenedicarboxylic acid, aromatic carboxylic acids and their anhydrides, such as phthalic acid in its isomer forms, also tri- and tetracarboxylic acids and their anhydrides, such as trimellitic acid, pyromellitic acid, polycarboxylic acids partially esterified with allyl alcohol, examples being monoallyl trimellitate and diallyl pyromellitate; particular

importance is attached to benzophenonecarboxylic acids, since by way of such carboxylic acids it is possible to incorporate, copolymerically, structures which can be excited by UV light.

- 5 Examples of suitable hydroxy components are alkoxyated or nonalkoxyated, at least dihydric, aliphatic and/or cycloaliphatic alcohols such as ethylene glycol, propylene glycol, polyethylene glycols, polypropylene glycols, butanediol isomers, hexanediol, trimethylolpropane, pentaerythritol, neopentyl glycol, cyclohexanedimethanol, bisphenol A, hydrogenated bisphenol A, OH-polyfunctional
 10 polymers, such as hydroxyl-modified polybutadienes or hydroxyl-bearing polyurethane prepolymers, glycerol, mono- and diglycerides of saturated and unsaturated fatty acids, especially monoglycerides of linseed oil or sunflower oil. Also suitable are unsaturated alcohols, such as polyfunctional hydroxy compounds etherified (partially) with allyl alcohol, examples being trimethylolethane
 15 monoallyl ether, trimethylolethane diallyl ether, trimethylolpropane monoallyl ether, trimethylolpropane diallyl ether, pentaerythritol monoallyl ether, pentaerythritol diallyl ether, 2-butene-1,4-diol and alkoxyated 2-butene-1,4-diol.

- If monofunctional substances are employed to regulate the molecular weight, they
 20 are preferably monofunctional alcohols, such as ethanol, propanol, butanol, hexanol, decanol, isodecanol, cyclohexanol, benzyl alcohol, or allyl alcohol. In the context of the present invention, the term polyesters includes polycondensates which in addition to the ester groups feature amide and/or imide groups, as are obtained by the additional use of amino compounds. Polyesters modified in this
 25 way are known, for example, from DE-A-15700273 and DE-A-17200323. These polyesteramides or polyesterimides may in many cases meet certain requirements - in terms, for example, of heat stability, chemical resistance, hardness and scratch resistance - better than do pure polyesters.

- 30 The double bonds of the unsaturated polyesters used can also be subjected to an addition reaction with DCPD, thereby making it possible to incorporate endomethylenetetrahydrophthalic acid structures of the formula IV.



IV

- 10 -

These endomethylenetetrahydrophthalic acid structures can be present at the chain-internal double bonds of the polyesters and/or at terminal double bonds, as are introduced, for example, by way of substances of the formula III.

5 Groups a) and b) of the invention can be introduced by cocondensation and/or by polymer-analogous reactions on polyesters with functional groups. Examples of cocondensations are the combined use of trimethylolpropane diallyl and monoallyl ethers, pentaerythritol diallyl and monoallyl ethers, and 2-butene-1,4-diol, alkoxylated 2-butene-1,4-diol and allyl alcohol.

10

Examples of polymer-analogous reactions on polyesters with functional groups are reactions of addition onto incompletely condensed, linear and/or branched, prepolymeric polyester resins which possess free carboxyl groups and free OH groups. These resins can be reacted at the carboxyl groups with unsaturated glycidyl compounds and vinyl ethers. Preferably, first of all, the free carboxyl groups are reacted with unsaturated glycidyl compounds in order to prevent acid-catalyzed polymerization of the vinyl ethers. Examples of suitable unsaturated glycidyl compounds are glycidyl (meth)acrylate, glycidyl undecenoate, (meth)-acrylicization products of polyfunctional epoxy resins and/or allyl glycidyl ether, in which case preferably glycidyl (meth)acrylate is added on. Then, following these reactions, the hydroxyl groups are reacted with diisocyanates and hydroxyvinyl ethers.

15

20

It is preferred, however, first to react diisocyanates having isocyanate groups of different reactivity, such as isophorone diisocyanate, with half the equivalent amount of hydroxyvinyl ethers and then to react these reaction products with the prepolymeric polyesters. In the case of said reactions, hydroxyl-functional acrylates may also be used, in addition to the hydroxyvinyl ethers. In the manner described lastly, purely hydroxyl-functional prepolymeric polyesters can also be reacted with hydroxyvinyl ethers and hydroxyl-functional compounds having groups b), examples being hydroxyalkyl (meth)acrylates or allyl alcohol. The introduction of groups of the formula I in this way is likewise possible through the concomitant use of commercially available dihydrodicyclopentadienol. It is preferred, however, to introduce groups of the formula I into polyesters by the cocondensation of the monoesters of maleic acid with dihydrodicyclopentadienol, of the formula III. These monoesters are obtainable in an elegant reaction from maleic anhydride (MAA), water and dicyclopentadiene (DCPD) or by a direct addition reaction of

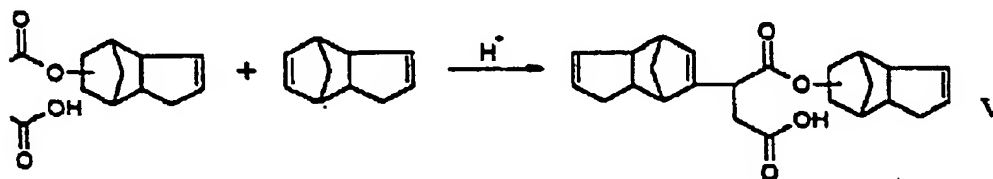
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DCPD with MAA. In addition, it is possible to add DCPD directly onto other acids and/or acidic polyesters. These reactions, however, are usually less elegant and require catalysis with, for example, BF_3 etherate.

Furthermore, it is known from US-A-5,252,682, for example, that in the reaction of DCPD and MAA there may to a minor extent be side reactions in accordance with the formula scheme V. These byproducts likewise serve to introduce structures of the formula I.



Hydroxyl-functional compounds for introducing groups of the formula I are dihydrocyclopentadienyl alcohol and, preferably, the adducts of DCPD with glycols, which are obtainable inexpensively by acid catalysis in accordance with the formula scheme VI.



Polyacrylate resins, which in accordance with the invention are functionalized with groups a) and b), constitute a further important class of polymer according to the invention and are obtained by copolymerizing acrylic esters, alone or with further copolymerizable compounds.

A preferred method of preparing polyacrylates is that of solvent-free, free-radical bulk polymerization in a stirred reactor, at atmospheric or superatmospheric pressure or, with particular preference, in continuous through-flow reactors at temperatures above the melting point of the resultant polymers, preferably above 140°C .

This method produces polyacrylates of low molecular weight and narrow molecular weight distribution, which is highly desirable in the case of powder coating materials, in particular, owing to the resultant narrower melting range and the

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lower melt viscosity. In addition, bulk polymerization does away with the need to remove an auxiliary solvent, and it is possible to incorporate pigments and coating auxiliaries directly into the melt. Alternatively, the polyacrylate resins of the invention can be prepared in solvents.

5

Examples of components for synthesizing polyacrylate resins are the known esters of acrylic and methacrylic acid with aliphatic, cycloaliphatic, araliphatic and aromatic alcohols of 1 to 40 carbon atoms, such as, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, amyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, tridecyl (meth)acrylate, cyclohexyl (meth)acrylate, methylcyclohexyl (meth)acrylate, benzyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, furfuryl (meth)acrylate and the esters of 3-phenylacrylic acid and the various isomeric forms thereof, such as methyl cinnamate, ethyl cinnamate, butyl cinnamate, benzyl cinnamate, cyclohexyl cinnamate, isoamyl cinnamate, tetrahydrofurfuryl cinnamate, furfuryl cinnamate, acrylamide, methacrylamide, methylolacrylamide, methylolmethacrylamide, acrylic acid, methacrylic acid, 3-phenylacrylic acid, hydroxyalkyl (meth)acrylates, such as ethyl glycol mono(meth)acrylate, butyl glycol mono(meth)acrylates, hexanediol mono(meth)acrylate, glycol ether (meth)acrylates, such as methoxyethyl glycol mono(meth)acrylate, ethyloxyethyl glycol mono(meth)acrylate, butyloxyethyl glycol mono(meth)acrylate, phenyloxyethyl glycol mono(meth)acrylate, glycidyl acrylate, glycidyl methacrylate, and amino (meth)acrylates, such as 2-aminoethyl (meth)acrylate.

Further suitable components are free-radically copolymerizable monomers, such as styrene, 1-methylstyrene, 4-tert-butylstyrene, 2-chlorostyrene, vinyl esters of fatty acids of 2 to 20 carbon atoms, such as vinyl acetate, vinyl propionate, vinyl ethers of alkanols of 2 to 20 carbon atoms, such as vinyl isobutyl ether, vinyl chloride, vinylidene chloride, vinyl alkyl ketones, dienes, such as butadiene and isoprene, and also esters of maleic acid and crotonic acid. Further suitable monomers are cyclic vinyl compounds, such as vinylpyridine, 2-methyl-1-vinylimidazole, 1-vinylimidazole, 5-vinylpyrrolidone and N-vinylpyrrolidone. Monomers with allylic unsaturation can also be employed, examples being allyl alcohol, allylalkyl esters,

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monoallyl phthalate and allyl phthalate. Acrolein and methacrolein, and polymerizable isocyanates, are also suitable.

5 Vinyl ether groups a) and coreactive groups b) can be incorporated by copolymerization during the preparation of the polyacrylates or, preferably, by subsequent polymer-analogous reaction. Examples of readily polymerizable compounds which additionally are reactive with vinyl ethers are copolymerizable epoxy compounds, such as glycidyl (meth)acrylate or dihydrodicyclopentadienol (meth)acrylate, dihydrodicyclopentadienyl ethacrylate and dihydrodicyclopentadienyl cinnamate. The epoxy groups of copolymerized glycidyl (meth)acrylate are able to polymerize with vinyl ethers directly by a cationic mechanism, but are also anchor groups for polymer-analogous functionalization reactions of the polymers, for the purpose, for example, of introducing acrylic double bonds by reaction with (meth)acrylic acid and/or for introducing vinyl ether groups by reaction with amino vinyl ether compounds, such as, for example, diethanolamine divinyl ether.

20 Dihydrodicyclopentadienyl groups of copolymerized dihydrodicyclopentadienyl compounds can be crosslinked or copolymerized directly with vinyl ether groups by initiation with UV irradiation and/or thermally, using free-radical donor compounds.

25 In principle, the invention is not restricted to the abovementioned classes of polymer. It can be an advantage to use mixtures of different polymer classes. In this case, particular preference is given to mixtures of relatively soft and elastic polyurethane resins or polyacrylate resins, which per se do not form blocking-resistant powders, with hard polyester resins having good blocking resistance properties.

30 The various functionalization methods referred to can be carried out in arbitrary combination in uniform polymeric precursors or mixtures of different polymeric precursors. This provides a kind of modular system which permits the properties of the powder coating materials to be adapted to a very wide variety of requirements.

35 The substances of the invention can also be mixed with further, preferably solid compounds which are reactive with the vinyl ether groups a) and/or with the groups b) that are coreactive with said groups a), examples of such compounds being

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unsaturated, preferably partially crystalline polyesters, monomeric and/or polymeric acrylates, vinyl esters, vinyl ethers, allyl esters and allyl ethers, e.g., polyester acrylates, polyether acrylates, polyurethane acrylates and polyurethane vinyl ethers. In such mixtures as well, the disruptive oxygen inhibition of the surface is advantageously suppressed.

The substances of the invention can comprise copolymerically incorporated photoinitiators, as are set out in more detail further below.

10 The invention also provides formulations which comprise the substance of the invention. The formulation of the invention can comprise at least one compound which on heating or under high-energy irradiation provides free radicals and/or cations.

15 The invention also provides for uses of the formulation of the invention. These include its use as or in a binder for liquid coating systems, with or without the use of solvents, coating dispersions or powder coating materials.

20 When the formulations of the invention are used, such coating systems can be crosslinked with a surprisingly high reactivity and even without coinitiators exhibit no oxygen inhibition of the surface. Furthermore, they can be cured by baking with compounds which on heating produce free radicals.

25 These coating systems are cured with conventional photoinitiators of Norrish type I or II or with catalysts which on heating produce free radicals, such as peroxides, azo initiators or C-C-labile compounds, such as those of the pinacol type, for example. Furthermore, combinations featuring maleic and/or fumaric acid groups are in many cases curable in customary coat thicknesses by baking in air.

30 Particularly preferred photoinitiators are those which are bonded copolymerically. Examples of copolymeric photoinitiators which can be employed are copolymerizable derivatives of benzophenone and compounds which are known from EP-A-486 897, DE-A-38 20 463, DE-A-40 07 318 and which embrace in particular those compounds derived from aromatic or partially aromatic ketones and have thioxanthone structures. Copolymeric photoinitiators can also be incorporated by
35 the addition reaction of, for example, hydroxybenzophenone onto copolymerized epoxy compounds, such as glycidyl (meth)acrylate, for example. Polymers which

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have, for example, copolymerically bonded benzophenone groups, in particular, can be crosslinked with high sensitivity by UV. This reactivity is further enhanced if at the same time structural units of the formula I are present as functional group b).

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If the coating systems comprising the formulations of the invention include compounds which on heating or under high-energy radiation provide free radicals and/or cations, curing can take place by purely thermal means, for example, by baking in air, and/or by means of high-energy radiation, with initiators, such as peroxides, azo initiators or C-C-labile compounds.

10

Such coating systems can be used for coating a wide variety of surfaces. These surfaces can, quite generally, be flat or shaped, fibrous or particulate substrates of any desired materials, such as metal, wood, plastic, glass, ceramic, silicon, etc. The selection of the polymeric substructure to be combined and of the coreactive groups b) for the binder of the respective powder coating material takes place in accordance with the requirements of the intended use in such a way that the finished coatings meet the set requirements. The basic principles governing the selection of the polymeric substructure and the coreactive groups b) of the constituent monomers for establishing the basic properties of the coating materials are known to the polymer chemist and to the skilled worker.

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The requirements imposed on the finished coatings can be very different. For clear topcoats of automotive metallic finishes, for example, the utmost yellowing resistance and weathering stability, scratch resistance and gloss retention are called for along with a high level of hardness.

25

In the case of a coil coating material, i.e., a coating material with which metal strips are coated, then wound up and processed further later, with deformation, important parameters are very high elasticity and adhesion. The price of the monomers may also be a selection criterion if for certain applications high quality of the coatings is not a particular requirement but a low price is.

30

For example, the hardness, glass transition temperature and softening point of the polymers can be increased by using higher proportions of "hard" monomers, such as styrene or the (meth)acrylates of C1 to C3 alcohols, whereas, for example, butyl acrylate, ethylhexyl acrylate or tridecyl acrylate, as "soft" monomers, attenuate

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these properties but at the same time improve the elasticity. Minor proportions of (meth)acrylic acid or (meth)acrylamide improve the adhesion.

The influences of the molecular weight, the molecular weight distribution, the control of the polymerization by means of regulators, temperature sensing and catalyst selection are fundamentally known.

Monomers which in addition to the double bond carry further functional groups can also be used for an additional heat-activatable crosslinking reaction. In general, however, they are employed in minor amounts in which they improve, for example, the adhesion, electrostatic chargeability, flow behavior of the coating materials, and surface smoothness. Derivatives of the 3-phenylacrylic acids, moreover, as incorporated stabilizers, improve the weathering stability of the coatings.

The coating formulations may additionally comprise pigments and/or customary coating auxiliaries, such as leveling assistants, devolatilizing assistants, other wetting agents and dispersants, dyes, and fillers. Also possible are aqueous dispersions of the coating powders, known as powder slurries, in order to open up application in liquid form to the powder coating materials.

It is also possible to prepare aqueous dispersions, for example, by (partial) neutralization of polymer-bound amino groups or dispersion with the aid of protective colloids. In this case it is advantageous to establish a pH of > 7 in order to prevent acid-catalyzed hydrolysis of the vinyl ethers.

The invention also provides for the use of the formulation of the invention as or in adhesives. These adhesives can be applied from the melt, as liquid systems, or as a solution or dispersion in appropriate solvents or water. In this case too, curing can be carried out thermally and/or with high-energy radiation, preferably UV light.

In addition, the formulation of the invention can be used in the form of casting and impregnating compositions for electronics and/or electrical engineering. In this case, the formulations can be applied from the melt, as systems liquid at room temperature, or as solutions or dispersions in appropriate solvents or water. Here again, curing can be carried out thermally and/or with high-energy radiation, preferably UV light.

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A further use in accordance with the invention relates to the preparation of formulations for producing moldings, which can comprise fibrous reinforcing materials in flat formation and/or present randomly. Examples of possible such reinforcing materials are glass fibers and/or other fillers and reinforcing substances.

5 Pigments may also be included.

In the text below the intention is to illustrate the invention further with reference to examples:

10 **Examples**

Example 1: Polyurethane with vinyl ether and acrylate groups

387 g of hexamethylene diisocyanate (2.3 mol)

15 185 g of vinyl cyclohexyl ether

1.50 g of tert-butylcresol

0.75 g of hydroquinone monomethyl ether

0.15 g of phenothiazine

0.6 g of dibutyltin dilaurate

20 are weighed out into a stirring flask equipped with feed vessel and reflux condenser. The mixture is heated to 80°C under a gentle stream of nitrogen and over an hour a dissolved mixture of

90 g of 1,4-butanediol (1 mol)

25 174 g of hydroxyethyl acrylate (1.5 mol)

58 g of 1,4-butanediol monovinyl ether (0.5 mol)

30 g of trimethylolpropane (0.22 mol)

50 g of vinyl cyclohexyl ether (solvent)

is added dropwise. There is an exothermic reaction. The temperature is held at
30 from 80 to 90°C by gentle cooling and following the end of the addition is held at 80°C for a further hour. Thereafter, isocyanate can no longer be detected in the IR spectrum. Cooling gives a waxy, pale yellowish substance having a melting point of about 80°C.

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Example 2: Polyurethane with vinyl ether and acrylate groups

289 g of Basonat HI 100 (trimerized hexamethylene diisocyanate with 21.8% NCO)
 5 111 g of vinyl cyclohexyl ether
 1 g of tert-butylcresol
 0.5 g of hydroquinone monomethyl ether
 0.1 g of phenothiazine
 0.4 g of dibutyltin dilaurate (as catalyst)
 10 are weighed out into a stirring flask equipped with feed vessel and reflux condenser. The mixture is heated to 80°C under a gentle stream of nitrogen and over an hour a dissolved mixture of
 11.4 g of 1,4-butanediol (0.125 mol)
 87 g of hydroxyethyl acrylate (0.75 mol)
 15 58 g of 1,4-butanediol monovinyl ether (0.5 mol)
 is added dropwise. There is an exothermic reaction. The temperature is held at from 80 to 90°C by gentle cooling and following the end of the addition is held at 80°C for a further hour. Thereafter, isocyanate can no longer be detected in the IR spectrum. Cooling gives a clear, colorless resin solution.

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Example 3: Polyacrylate with aminovinyl ether and acrylate groups

486 g of butyl acetate
 are weighed out into a stirring flask equipped with feed vessel and reflux
 25 condenser, and this initial charge is brought to 85°C. Then, as feed stream I,
 300 g of methyl methacrylate
 200 g of glycidyl methacrylate (1.41 mol)
 300 g of butyl acrylate
 200 g of ethyl hexyl acrylate and
 30 10 g of mercaptoethanol
 are added over 90 minutes and, as feed stream II,
 30 g of 2,2'-azobis(2-methylbutyronitrile)
 Wako-Starter V59, dissolved in
 190 g of butyl acetate,
 35 are added over 120 minutes. Polymerization is continued at 85°C for 3 hours, after which the batch is cooled to 50°C and
 67.6 g of acrylic acid (0.94 mol)

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0.7 g of tert-butylcresol
0.35 g of hydroquinone monomethyl ether
0.07 g of phenothiazine and
0.7 g of dimethylaminopyridine
5 are added and the mixture is stirred at 95 to 100°C for 8 hours. Thereafter, a resin solution with an acid number of 6.2 is obtained. This solution is cooled to 60°C and
74 g of diethanolamine divinyl ether (0.47 mol)
are added dropwise over one hour. There is a slightly exothermic reaction. After a
10 further 3 hours at 80°C, the mixture is cooled. This gives a viscous, yellowish resin solution.

Example 4: Polyacrylate with aminovinyl ether and dihydrodicyclopentadienyl groups

15 486 g of butyl acetate
are weighed out into a stirring flask equipped with feed vessel and reflux condenser, and this initial charge is brought to 85°C. Then, as feed stream I,
200 g of methyl methacrylate
20 106.5 g of glycidyl methacrylate (0.75 mol)
300 g of butyl acrylate
200 g of ethyl hexyl acrylate
100 g of dihydrodicyclopentadienyl acrylate and
10 g of mercaptoethanol
25 are added over 90 minutes and, as feed stream II,
30 g of 2,2'-azobis(2-methylbutyronitrile)
Wako-Starter V59, dissolved in
180 g of butyl acetate,
are added over 120 minutes. Polymerization is continued at 85°C for 3 hours, after
30 which the batch is cooled to 60°C and
118 g of diethanolamine divinyl ether (0.75 mol)
are added dropwise over one hour, with a slightly exothermic reaction. After a
further 3 hours at 80°C, the result is a viscous, pale yellowish resin solution.

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Example 5: Polyacrylate with aminovinyl ether, acrylate and dihydrodi-cyclopentadienyl groups

486 g of butyl acetate
5 are weighed out into a stirring flask equipped with feed vessel and reflux condenser, and this initial charge is brought to 85°C. Then, as feed stream I,
200 g of methyl methacrylate
100 g of dihydrodicyclopentadienyl acrylate
200 g of glycidyl methacrylate (1.41 mol)
10 300 g of butyl acrylate
200 g of ethyl hexyl acrylate and
10 g of mercaptoethanol
are added over 90 minutes and, as feed stream II,
30 g of 2,2'-azobis(2-methylbutyronitrile)
15 Wako-Starter V59, dissolved in
180 g of butyl acetate,
are added over 120 minutes. Polymerization is continued at 85°C for 3 hours, after which the batch is cooled to 50°C and
67.6 g of acrylic acid (0.94 mol)
20 0.7 g of tert-butylcresol
0.35 g of hydroquinone monomethyl ether
0.07 g of phenothiazine and
0.7 g of dimethylaminopyridine
are added and the mixture is stirred at 95 to 100°C for 8 hours. Thereafter, a resin
25 solution with an acid number of 6.2 is obtained. This solution is cooled to 60°C and
74 g of diethanolamine divinyl ether (0.47 mol)
are added dropwise over one hour. There is a slightly exothermic reaction. After a
further 3 hours at 80°C, the mixture is cooled. This gives a viscous, yellowish resin
30 solution.

Comparative Example 1: Comparative Example: Polyacrylate with acrylate groups only

35 486 g of butyl acetate
are weighed out into a stirring flask equipped with feed vessel and reflux condenser, and this initial charge is brought to 85°C. Then, as feed stream I,

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- 300 g of methyl methacrylate
 200 g of glycidyl methacrylate (1.41 mol)
 300 g of butyl acrylate
 200 g of ethyl hexyl acrylate and
 5 10 g of mercaptoethanol
 are added over 90 minutes and, as feed stream II,
 30 g of 2,2'-azobis(2-methylbutyronitrile)
 Wako-Starter V59, dissolved in
 180 g of butyl acetate,
 10 are added over 120 minutes. Polymerization is continued at 85°C for 3 hours, after
 which the batch is cooled to 50°C and
 101 g of acrylic acid (1.39 mol)
 0.7 g of tert-butylcresol
 0.35 g of hydroquinone monomethyl ether
 15 0.07 g of phenothiazine and
 0.7 g of dimethylaminopyridine
 are added and the mixture is stirred at 95 to 100°C for 8 hours. After cooling, a
 clear, viscous resin solution with an acid number of 7.9 is obtained.

20 Test coating materials

L1	100 g B1 + 50 g TEGDVE	+ 5 g BDMK
L2	100 g B1 + 50 g HDA	+ 5 g BDMK
L3	100 g B2	+ 3 g BDMK
L4	100 g B2 + 50 g TEGDVE	+ 5 g BDMK
L5	100 g B2 + 50 g HDA	+ 5 g BDMK
L6	156 g B3 (about 100 g resin content)	+ 3 g BDMK
L7	156 g B3 (about 100 g resin content) + 50 g TEGDVE	+ 3 g BDMK
L8	156 g B3 (about 100 g resin content) + 50 g HDA	+ 3 g BDMK
L9	156 g B4 (about 100 g resin content)	+ 3 g BDMK
L10	156 g B4 (about 100 g resin content) + 50 g TEGDVE	+ 3 g BDMK
L11	156 g B4 (about 100 g resin content) + 50 g HDA	+ 3 g BDMK
25 L12	156 g B5 (about 100 g resin content)	+ 3 g BDMK

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L13 156 g B5 (about 100 g resin content) + 50 g TEGDVE + 3 g BDMK

L14 156 g B5 (about 100 g resin content) + 50 g HDA + 3 g BDMK

VL 162 g VB1 (about 100 g resin content) + 3 g BDMK

1

VL 162 g VB1 (about 100 g resin content) + 50 g TEGDVE + 3 g BDMK

2

VL 162 g VB1 (about 100 g resin content) + 50 g HDA + 3 g BDMK

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BDMK = benzil dimethyl ketal (photoinitiator)

5 TEGDVE = triethylene glycol divinyl ether

HDA = hexanediol diacrylate

The test coating materials were formulated, and the test panels produced, in a UV-shielded laboratory. The constituents of the test coating materials were pre-mixed in glass bottles using a stirring spatula, and these mixtures were stored in a drying cabinet at 50°C for one hour and then thoroughly stirred again. After cooling to room temperature, clear viscous solutions resulted in all cases. The solutions were then applied using a coating bar with a gap height of 60 µm to degreased, bright steel panels. The panels with the solutions L6 to L14 and VL1 to VL3 were then stored overnight in a vacuum drying cabinet at 40°C to remove the solvent, butyl acetate. Thereafter, liquid viscous resin films are present on all test panels. The panels were then irradiated under a UV mercury vapor lamp having an emission maximum at about 365 nm and an energy output of 19 mJ/cm² in the plane of exposure until the films obtained were unattacked after 10 minutes of subjection to a cotton pad wetted with acetone. If surface inhibition of the films was observed, then the uncrosslinked, acetone-soluble layer present in that case was first of all wiped off and the swellability of the underlying, crosslinked layer was assessed.

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Test findings

<u>Coating material</u>	<u>Finding after UV irradiation</u>
L1	30 s: acetone resistant, no surface inhibition*
L2	60 s: acetone resistant, no surface inhibition
L3	90 s: acetone resistant, no surface inhibition
L4	30 s: acetone resistant, no surface inhibition
L5	60 s: acetone resistant, no surface inhibition
L6	90 s: acetone resistant, no surface inhibition
L7	30 s: acetone resistant, no surface inhibition
L8	60 s: acetone resistant, no surface inhibition
L9	120 s: acetone resistant, no surface inhibition
L10	30 s: acetone resistant, no surface inhibition
L11	60 s: acetone resistant, no surface inhibition
L12	30 s: acetone resistant, no surface inhibition
L13	30 s: acetone resistant, no surface inhibition
L14	30 s: acetone resistant, no surface inhibition
VL1	300 s: acetone resistant with tacky surface inhibition
VL2	240 s: acetone resistant, no surface inhibition
VL3	240 s: acetone resistant with tack-free surface inhibition

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10 * Surface inhibition: beneath a thin tacky or tack-free surface layer which remains uncrosslinked and soluble in acetone, the layers are insoluble in acetone.

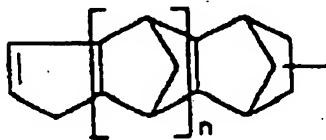
The examples show that the approach in accordance with the invention achieves extremely high UV sensitivity and prevents oxygen inhibition of the surface.

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We claim:

1. A substance which has an oligomeric or polymeric substructure and is curable thermally and/or by means of high-energy radiation and which comprises in each case terminally and/or laterally at least one vinyl ether group a) and at least one group b) which is different from the vinyl ether groups a) but is coreactive with said groups a), there being on average at least one vinyl ether group a) and one coreactive group b) per oligomer or polymer molecule.
2. A substance as claimed in claim 1, wherein the coreactive groups b) are copolymerizable with the vinyl ether groups a).
3. A substance as claimed in claim 1 or 2, wherein the oligomeric or polymeric substructure is formed by C-C linkages which have double and/or triple bonds and/or are selected from ester, ether, urethane, amide, imide, imidazole, ketone, sulfide, sulfone, acetal, urea, carbonate and siloxane linkages.
4. A substance as claimed in any of claims 1 to 3, wherein the oligomeric or polymeric substructure is linear, branched, annular or dendrimeric.
5. A substance as claimed in any of claims 1 to 4, wherein the coreactive groups b) are selected from maleate, fumarate, itaconate, (meth)acrylate, allyl, epoxy, alkenyl, cycloalkenyl, vinylaryl and cinnamate groups and/or structural units of the formula I.



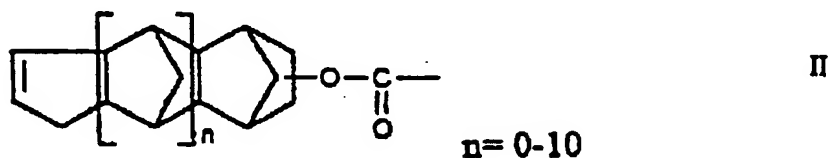
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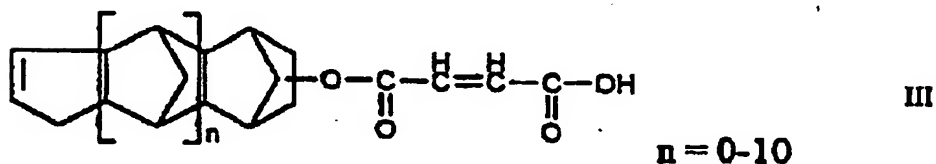
6. A substance as claimed in claim 5, wherein the structural units of the formula I in the coreactive groups b) are incorporated in the form of esters

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of (oligo)dihydrodicyclopentadienol with monofunctional or polyfunctional carboxylic acids of the formula II.



- 5
7. A substance as claimed in claim 5 or 6, wherein the structural units of the formula I and II in the coreactive groups b) are incorporated in the form of (oligo)dihydrodicyclopentadienol monoesters of maleic acid and fumaric acid, of the formula III, and the link to the substructure is produced by way of ester groups and/or amide groups.
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8. A substance as claimed in any of claims 1 to 7 which comprises a copolymerically incorporated photoinitiator.
9. A formulation which comprises a substance as claimed in any of claims 1 to 8.
- 20
10. A formulation as claimed in claim 9, which comprises at least one compound which on heating or under high-energy radiation provides free radicals and/or cations.
- 25
11. The use of a formulation as claimed in claim 9 or 10 as or in a binder for liquid coating systems, with or without the use of solvents, or coating dispersions.
12. The use of a formulation as claimed in claim 9 or 10 as or in a binder for powder coating materials.
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13. The use of a formulation as claimed in claim 11 or 12, wherein pigments and/or customary coatings auxiliaries are additionally present.
14. The use of a formulation as claimed in claim 9 or 10 as or in adhesives.
15. The use of a formulation as claimed in claim 9 or 10 as or in casting and impregnating compositions for electronics and/or electrical engineering.
16. The use of a formulation as claimed in claim 9 or 10 for the production of moldings.

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